Anionic Monoazo Dyes

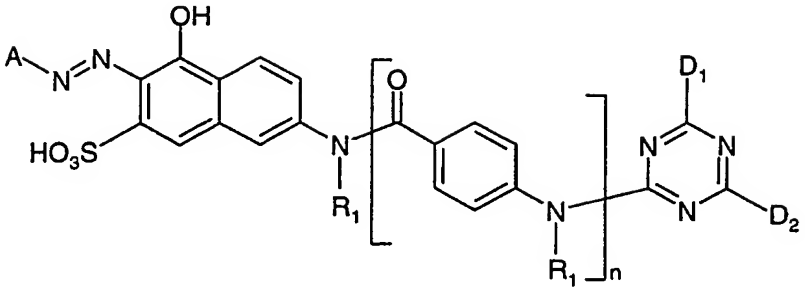
The present invention relates to novel anionic monoazo dyes, a process for their preparation and the use of these dyes for dyeing natural or synthetic materials, in particular, paper.

Monoazo dyes based on coupling reactions of diazotised aromatic amines with 1,3,5-triazinyl-l-acid derivatives have previously been described, for example, in EP 548,795, solely in the form of reactive dyes for cotton.

Furthermore, in recent years, the use of concentrated aqueous solutions of dyes has gained importance because of the advantages possessed by such solutions when compared with dyes in powder form. The use of solutions avoids the difficulties associated with dust formation and releases the user from the time-consuming and frequently difficult dissolving of the dye powder in water. The use of concentrated solutions was also prompted by the development of continuous dyeing processes for paper, since it is convenient in these processes to meter the solution directly into the pulp stream or to add it at some other suitable point of the papermaking process.

Surprisingly, it has now been found that anionic dyes based on this chromophoric system are especially valuable for use in dyeing paper, since they possess highly desirable yellowish-red shades. Such shades of dyeings have, hitherto, only been attainable with difficulty, since no single dyestuff has been available and it has been necessary to incorporate mixtures of yellow and red dyes to obtain such shades. Furthermore, the dyes of the present invention exhibit high degrees of exhaustion under particular dyeing conditions, resulting in dyeings of exceptional brilliance not obtainable by the use of mixtures. In addition the dyes of the invention exhibit excellent water-solubility, thus enabling the ready preparation of concentrated liquid selling grades.

Accordingly, the invention relates to compounds of the formula



(1),

in which

A represents a 1- or 2-naphthyl residue, which is substituted by a total of one or two sulphonic

and/or carboxylic acid groups, preferably a 1- or 2-naphthyl mono- or disulphonic acid or a 1- or 2-naphthyl monocarboxylic acid residue,

R_1 represents hydrogen or C_1-C_4alkyl, each

D_1 and D_2, independently of the other, represent either

an amino acid residue resulting from removal of a hydrogen atom from the amino group of the amino acid or the residue

$-NR_2R_3$, in which each

R_2 and R_3, independently of the other, represent hydrogen, C_1-C_4alkyl, C_2-C_6alkyl which is substituted by hydroxy, halogen or cyano, phenyl which is unsubstituted or monosubstituted by hydroxy, halogen, SO_3H, C_1-C_4alkyl or C_1-C_4alkoxy or, alternatively,

R_2 and R_3, together with the nitrogen atom to which they are connected, complete a saturated, 5- or 6-membered ring which may contain, in addition to the nitrogen atom, one nitrogen or oxygen atom and which may be further substituted and

n is 0 or 1.

More preferred compounds of formula (1) are those in which

R_1 represents hydrogen

D_1 and D_2, independently of the other, is an amino acid residue residue resulting from removal of a hydrogen atom from the amino group of the amino acid and which is derived from glycine, alanine, serine, cysteine, phenylalanine, tyrosine (4-hydroxyphenylalanine), diiodotyrosine, tryptophan (β-indolylalanine), histidine ((β-imidazolylalanine), α-aminobutyric acid, methionine, valine (α-aminoisovaleric acid), norvaline, leucine (α-

aminoisocaproic acid), isoleucine (α-amino-β-methylvaleric acid), norleucine (α-amino-n-caproic acid), arginine, ornithine (α,δ-diaminovaleric acid), lysine (α,ε-diaminocaproic acid), aspartic acid (aminosuccinic acid), glutamic acid (α-aminoglutaric acid), threonine and hydroxyglutamic acid as well as mixtures and optical isomers thereof or from iminodiacetic acid, a residue

$-NR_2R_3$, in which each

R_2 and R_3, independently of the other, represent hydrogen, C_2-C_4hydroxyalkyl, phenyl, which is unsubstituted or monosubstituted by SO_3H or, alternatively, a morpholino, piperidino or pyrrolidino residue.

Especially preferred compounds of formula (1) are those in which

A represents a 1-naphthyl-2-, 3-, 4-, 5-, 6-, 7- or 8-sulphonic acid, a 2-naphthyl-1-, 5-, 6- or 7-sulphonic acid, a 2-naphthyl-1-, 3- or 6-carboxylic acid, a 1-naphthyl-3,8- or 4,8-disulphonic acid or a 2-naphthyl-1,5-, 3,6-, 4,8- or 6,8-disulphonic acid residue and each

D_1 and D_2, independently of the other, is an amino acid residue from which a hydrogen atom on the amino group has been removed and which is derived from glycine, alanine, serine, phenylalanine, aspartic acid (aminosuccinic acid) or glutamic acid (α-aminoglutaric acid), a residue

$-NR_2R_3$, in which each

R_2 and R_3, independently of the other, represent hydrogen, C_2-C_3hydroxyalkyl, phenyl, which is unsubstituted or monosubstituted by SO_3H or, alternatively, a morpholino residue.

Most especially preferred compounds of formula (1) are those in which

A represents a 1-naphthyl-2-, 3-, 4-, 5-, 6-, 7- or 8-sulphonic acid, a 2-naphthyl-1-, 5-, 6- or 7-sulphonic acid, a 2-naphthyl-1-, 3- or 6-carboxylic acid, a 1-naphthyl-3,8- or 4,8-disulphonic acid or a 2-naphthyl-1,5-, 3,6-, 4,8- or 6,8-disulphonic acid residue, most especially, when

n is 0, a 2-naphthyl-6- or 7-sulphonic acid residue and, when

n is 1, a 1-naphthyl-4-sulphonic acid, 2-naphthyl-6-sulphonic acid or a 2-naphthyl-1,5-disulphonic acid residue,

R_1 represents hydrogen and both

D_1 and D_2 represent the group $-NHCH_2CH_2OH$.

The sulphonic and/or carboxylic acid groups present in compounds of formula (1) may be present either in the form of the free acid or in the salt form, SO_3M and/or CO_2M. M is preferably one equivalent of a colourless cation, typically lithium, sodium, potassium, ammonium or the protonated form of a C_4-C_{12}trialkylamine, C_4-C_{12}diamine, C_2-C_{12}-alkanolamine or of a polyglycol amine, conveniently, triethanolamine trisglycol ether, or mixtures of such cationic species.

M as a protonated C_4-C_{12}trialkylamine may, for example, be a protonated N-ethyl-dimethylamine, N,N-diethylmethylamine, tri-n-propylamine, tri-n-butylamine, tri-isobutylamine, and, preferably, triethylamine or triisopropylamine.

M as a protonated C_4-C_{12}diamine may, for example, be ethylenediamine, or 1,3-diaminopropane, in which one or both nitrogen atoms are additionally substituted by one or two C_1-C_4alkyl radicals, preferably methyl or ethyl radicals. M is preferably an N,N-dialkylethylenediamine or N,N-dialkyl-1,3-diaminopropane. Illustrative examples are: N-ethylethylenediamine, N,N-dimethylethylenediamine, N,N'-dimethylethylenediamine, N,N-diethylethylenediamine, 3-dimethylamino-1-propylamine or 3-diethylamino-1-propylamine.

M as a protonated C_2-C_{12}alkanolamine may be the protonated form of a monoalkanolamine, dialkanolamine, monoalkanolmonoalkylamine, monoalkanoldialkylamine, dialkanolalkylamine or trialkanolamine or a mixture of different protonated alkanolamines. Illustrative examples are: protonated 2-aminoethanol, bis(2-hydroxyethyl)amine, N-(2-hydroxyethyl)dimethylamine, N-(2-hydroxyethyl)diethylamine, N,N-bis(2-hydroxyethyl)ethylamine or tris(2-hydroxyethyl)-amine.

Within the scope of the definitions of R_1 as C_1-C_4alkyl and R_2 and/or R_3 as C_1-C_4alkyl and/ or C_2-C_6alkyl which is substituted by hydroxy, halogen or cyano, these alkyl radicals may be branched or unbranched, for example, methyl, ethyl, n-propyl, isopropyl, n-butyl, sec-butyl, isobutyl, t-butyl, 2-ethylbutyl, n-pentyl, isopentyl, 1-methylpentyl, 1,3-dimethylbutyl or n-hexyl.

Similarly, C_1-C_4alkoxy may be, for example, methoxy, ethoxy, n-propoxy, isopropoxy, n-butoxy, sec-butoxy, isobutoxy or t-butoxy.

Halogen in the above formulae and radicals is iodine, bromine, fluorine or, especially, chlorine.

The dyes of formula (1) of the invention may be prepared by known methods, for example by

reacting the diazonium salt of an amine of the formula

$$A\text{-}NH_2 \quad (2)$$

with either 2-amino- or 2-C_1-C_4alkylamino-5-hydroxynaphthalene-7-sulphonic acid (where n=0) or with 2-(4-amino- or 4-C_1-C_4alkylaminobenzoyl)amino- or C_1-C_4alkylamino-5-hydroxynaphthalene-7-sulphonic acid (where n=1), reaction with cyanuric chloride and subsequent sequential reaction of the dichloro intermediate with amines D_1H and D_2H or , alternatively,
reacting 2-amino- or 2-C_1-C_4alkylamino-5-hydroxynaphthalene-7-sulphonic acid (where n=0) or 2-(4-amino- or 4-C_1-C_4alkylaminobenzoyl)amino- or C_1-C_4alkylamino-5-hydroxynaphthalene-7-sulphonic acid (where n=1) with cyanuric chloride,
followed by sequential reaction of the dichloro intermediate with amines D_1H and D_2H and, finally, reaction with the diazonium salt of the amine of formula (2), whereby A, D_1, D_2 and n are as previously defined, the latter procedure being preferred.

The dyes of the invention may be used to dye natural or synthetic materials, for example, cellulosic materials, carbonamide group containing materials such as polyamides, leather or glass fibres, but are particularly useful for dyeing paper. They are preferably used as a solid or liquid commercial form.

The pulverulent or granular form of the dye can be used particularly in batchwise pulp dyeing where the dye mixture, customarily in the form of a stock solution, is added in the pulper, in the beater or in the mixing chest. Preference is here given to using dye preparations which as well as the dye, may further include extenders, for example urea as solubilizer, dextrin, Glauber salt, sodium chloride and also dispersants, dustproofing agents and sequestrants, such as tetrasodium phosphate.

The present invention accordingly further provides solid dye preparations for dyeing paper comprising a compound of the formula (1) and, optionally, further auxiliaries.

The present invention further provides aqueous solutions, preferably concentrated solutions, for dyeing paper, comprising a compound of the formula (1), preferably in a concentration of from 5 to 30% by weight. Due to their excellent solubility in water, the dyes of formula (1) are particularly suitable for the preparation of such solutions.

The concentrated solutions preferably contain a low level of inorganic salts, which may be achieved, if necessary, by known methods, for example reverse osmosis.

The solutions may include further auxiliaries, for example solubilizers such as ε-caprolactam or urea, organic solvents, for example glycols, polyethylene glycols, dimethyl sulphoxide, N-methylpyrrolidone, acetamide, alkanolamines or polyglycolamines, which is a still further aspect of the invention.

In addition, the aqueous dye solutions of the present invention may be applied to paper by use of the so-called spraying technique.

The novel dyes of the invention dye paper in predominantly reddish shades with excellent degrees of exhaustion with high colour strength, whilst being sufficiently water-soluble to provide stable aqueous formulations without the need for large quantities of solubilizers. Furthermore, dyeings obtained exhibit high degrees of bleed- and light-fastness and are readily bleachable.

Furthermore, as a result of their high colour strength and water solubility, the novel dyes of the invention are suitable for use in the ink-jet printing method.

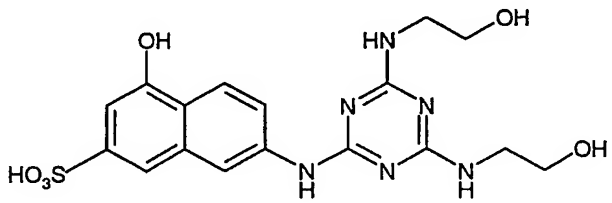
Consequently, one further aspect of the invention is paper, which is dyed with a compound of the formula (1), either in the form of a solid dye preparation, or an aqueous solution, as described above, as well as the use of the compounds of formula (1), according to the invention, for dyeing paper.

The following examples serve to illustrate the invention without intending to be restrictive in nature. Parts and percentages are by weight unless otherwise stated.

Examples

(A) Synthesis of Intermediate Triazinylamino-I-acid Derivatives

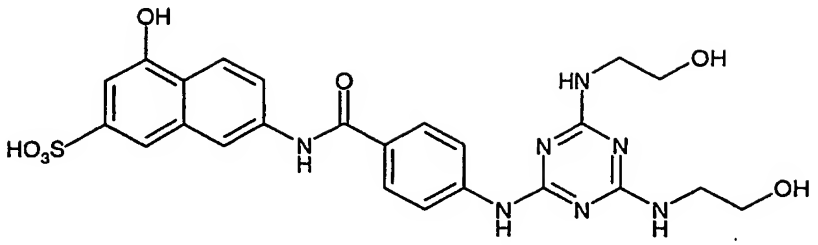
Example 1



(100a)

36.9g of cyanuric chloride are dissolved in 185ml of acetone and added to 200g of ice water at 0°C. At an initial temperature of 0-5°C and, subsequently, at 20°C, 28.7g of ethanolamine are added drop wise with stirring, the pH being maintained at 5.5-6.5. After 2.5 hours, the temperature is increased to 40-50°C and the pH maintained at 6.5-7.0 by addition of a total of 164ml of 2N aqueous sodium hydroxide solution. After a further 2 hours the consumption of sodium hydroxide ceases, the reaction mixture is stirred for a further 30 minutes, cooled to room temperature and the white suspension filtered. There are obtained 46.7g of the disubstituted intermediate which are suspended in 300g of water and treated with 47.9g of I-acid (7-amino-4-hydroxy naphthalene-2-sulphonic acid). The resulting beige suspension is heated to 85°C and the pH maintained at 3.0 by addition of a total of 94ml of 2N aqueous sodium hydroxide solution. After stirring for 3 hours reaction is complete, the pH is adjusted to 5.5 by addition of a further 8ml of 2N aqueous sodium hydroxide solution, the suspension cooled to room temperature and the precipitated solids filtered. There are obtained 77g of the compound of formula (100a).

Example 2

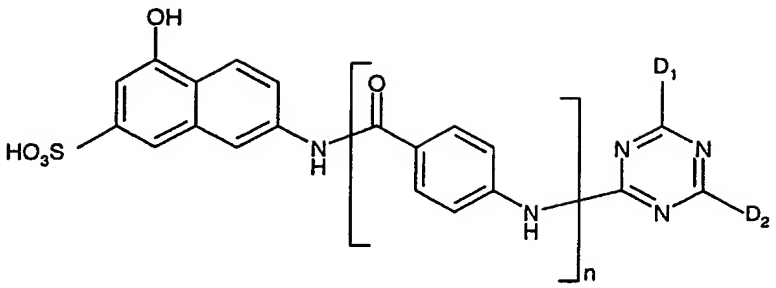


(100b)

36.9g of cyanuric chloride are dissolved in 185ml of acetone and added to 200g of ice water at 0°C. At an initial temperature of 0-5°C and, subsequently, at 20°C, 28.7g of ethanolamine are added drop wise with stirring, the pH being maintained at 5.5-6.5. After 2.5 hours, the temperature is increased to 40-50°C and the pH maintained at 6.5-7.0 by addition of a total of 164ml of 2N aqueous sodium hydroxide solution. After a further 2 hours the consumption of sodium hydroxide ceases, the reaction mixture is stirred for a further 30 minutes, cooled to room temperature and the white suspension filtered. There are obtained 46.7g of the disubstituted intermediate which are suspended in 300g of water and treated with 71.7g of p-aminobenzoyl-l-acid (7-(4-benzoylamino)-4-hydroxy naphthalene-2-sulphonic acid). The resulting beige suspension is heated to100°C and the pH maintained at 3.0 by addition of a total of 86ml of 2N aqueous sodium hydroxide solution. After stirring for 6 hours reaction is complete, the pH is adjusted to 5.7 by addition of a further 16ml of 2N aqueous sodium hydroxide solution, the suspension cooled to room temperature and the precipitated solids filtered. After purification by washing with dilute hydrochloric acid, there are obtained 80g of the compound of formula (100b).

Examples 3 - 150

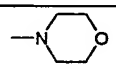
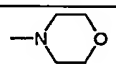
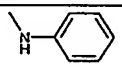
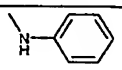
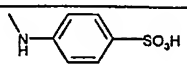
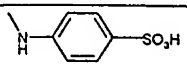
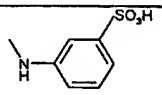
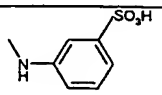
By proceeding in an analogous manner to that described in Examples 1 or 2, respectively, but replacing the ethanolamine by amines D_1H and/or D_2H, the following compounds of formula

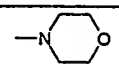
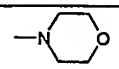
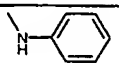
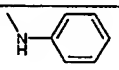
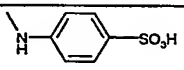
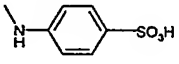
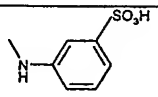
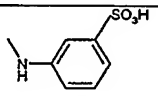
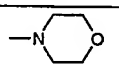
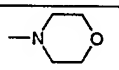
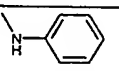
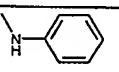
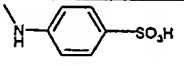
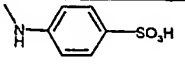


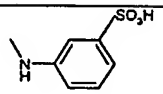
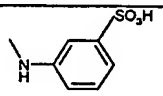
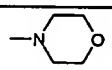
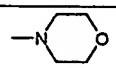
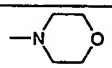
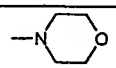
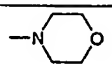
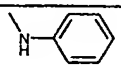
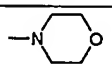
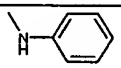
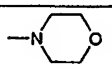
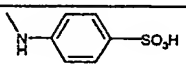
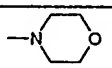
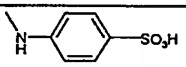
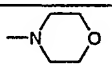
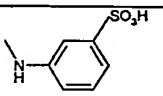
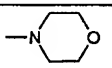
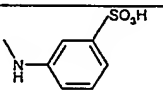
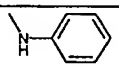
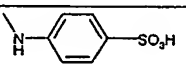
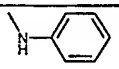
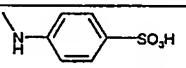
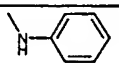
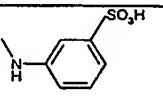
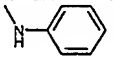
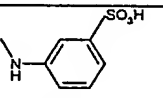
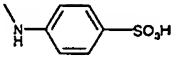
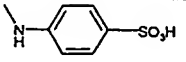
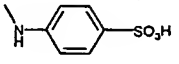
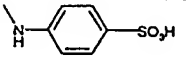
(3)

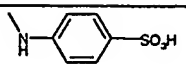
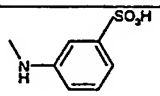
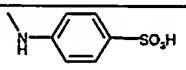
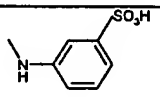
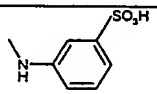
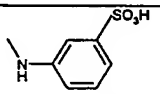
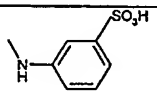
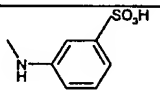
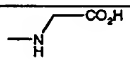
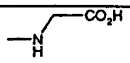
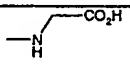
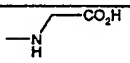
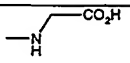
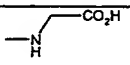
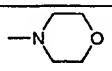
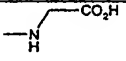
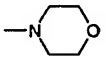
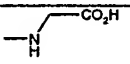
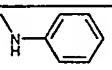
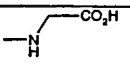
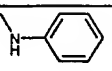
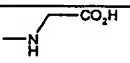
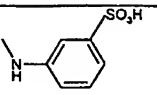
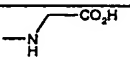
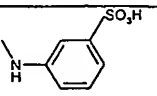
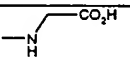
are obtained, as summarized in Table 1 below.

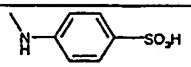
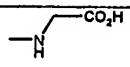
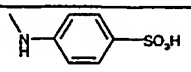
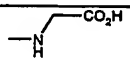
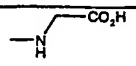
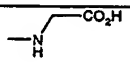
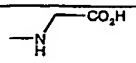
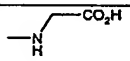
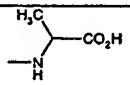
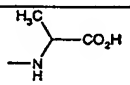
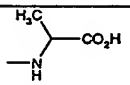
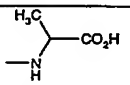
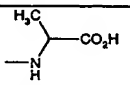
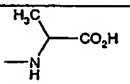
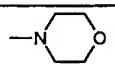
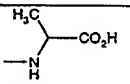
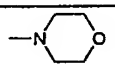
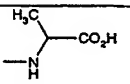
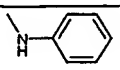
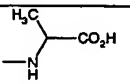
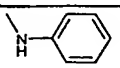
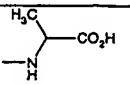
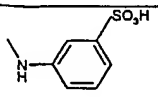
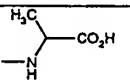
Table 1

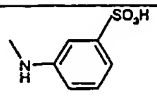
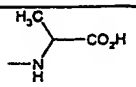
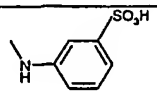
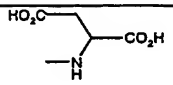
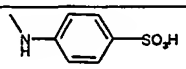
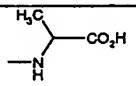
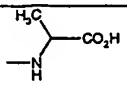
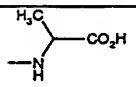
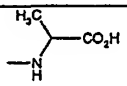
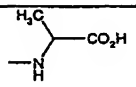
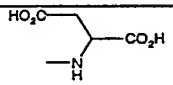
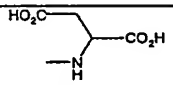
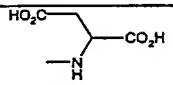
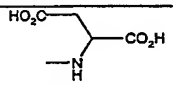
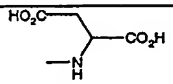
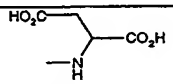
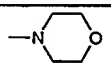
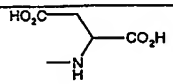
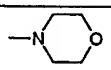
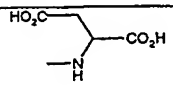
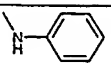
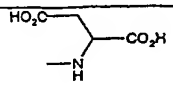
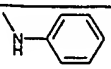
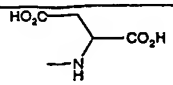
Example Nr.	Compound Nr.	D_1	D_2	n
3	(101a)	$-NHCH_2CH_2OH$	$-N(CH_2CH_2OH)_2$	0
4	(101b)	$-NHCH_2CH_2OH$	$-N(CH_2CH_2OH)_2$	1
5	(102a)	$-NHCH_2CH_2OH$	$-NHCH_2CH(CH)_3OH$	0
6	(102b)	$-NHCH_2CH_2OH$	$-NHCH_2CH(CH)_3OH$	1
7	(103a)	$-NHCH_2CH_2OH$		0
8	(103b)	$-NHCH_2CH_2OH$		1
9	(104a)	$-NHCH_2CH_2OH$		0
10	(104b)	$-NHCH_2CH_2OH$		1
11	(105a)	$-NHCH_2CH_2OH$		0
12	(105b)	$-NHCH_2CH_2OH$		1
13	(106a)	$-NHCH_2CH_2OH$		0
14	(106b)	$-NHCH_2CH_2OH$		1
15	(107a)	$-N(CH_2CH_2OH)_2$	$-N(CH_2CH_2OH)_2$	0

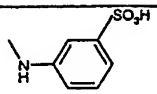
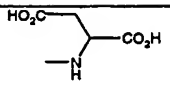
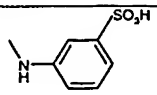
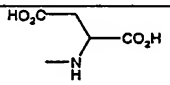
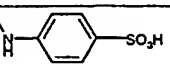
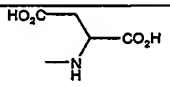
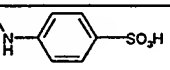
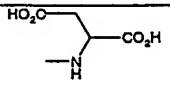
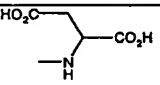
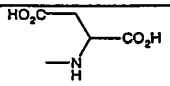
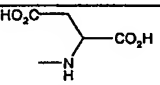
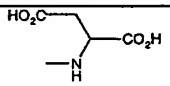
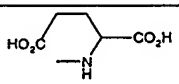
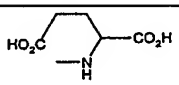
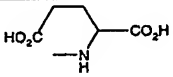
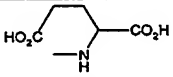
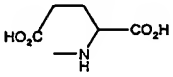
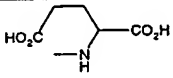
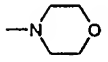
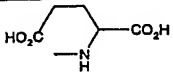
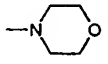
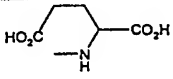
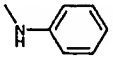
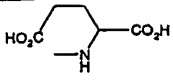
16	(107b)	$-N(CH_2CH_2OH)_2$	$-N(CH_2CH_2OH)_2$	1
17	(108a)	$-N(CH_2CH_2OH)_2$	$-NHCH_2CH(CH)_3OH$	0
18	(108b)	$-N(CH_2CH_2OH)_2$	$-NHCH_2CH(CH)_3OH$	1
19	(109a)	$-N(CH_2CH_2OH)_2$		0
20	(109b)	$-N(CH_2CH_2OH)_2$		1
21	(110a)	$-N(CH_2CH_2OH)_2$		0
22	(110b)	$-N(CH_2CH_2OH)_2$		1
23	(111a)	$-N(CH_2CH_2OH)_2$		0
24	(111b)	$-N(CH_2CH_2OH)_2$		1
25	(112a)	$-N(CH_2CH_2OH)_2$		0
26	(112b)	$-N(CH_2CH_2OH)_2$		1
27	(113a)	$-NHCH_2CH(CH)_3OH$	$-NHCH_2CH(CH)_3OH$	0
28	(113b)	$-NHCH_2CH(CH)_3OH$	$-NHCH_2CH(CH)_3OH$	1
29	(114a)	$-NHCH_2CH(CH)_3OH$		0
30	(114b)	$-NHCH_2CH(CH)_3OH$		1
31	(115a)	$-NHCH_2CH(CH)_3OH$		0
32	(115b)	$-NHCH_2CH(CH)_3OH$		1
33	(116a)	$-NHCH_2CH(CH)_3OH$		0
34	(116b)	$-NHCH_2CH(CH)_3OH$		1

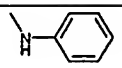
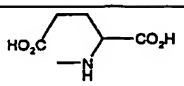
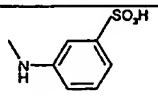
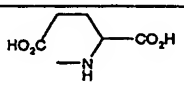
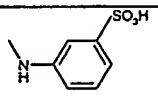
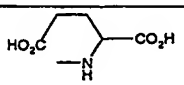
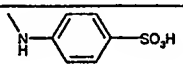
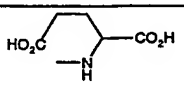
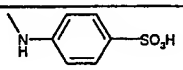
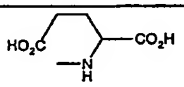
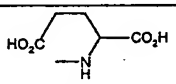
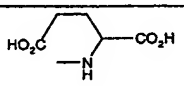
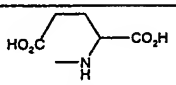
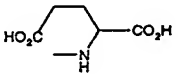
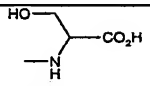
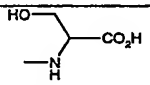
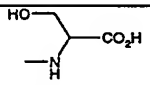
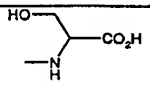
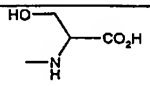
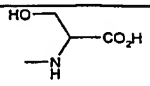
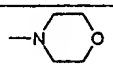
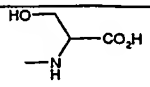
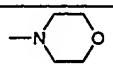
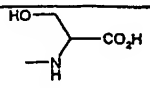
35	(117a)	$-NHCH_2CH(CH)_3OH$		0
36	(117b)	$-NHCH_2CH(CH)_3OH$		1
37	(118a)			0
38	(118b)			1
39	(119a)			0
40	(119b)			1
41	(120a)			0
42	(120b)			1
43	(121a)			0
44	(121b)			1
45	(122a)			0
46	(122b)			1
47	(123a)			0
48	(123b)			1
49	(124a)			0
50	(124b)			1

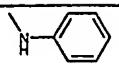
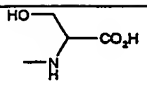
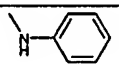
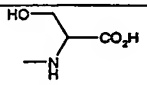
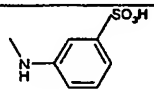
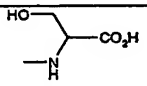
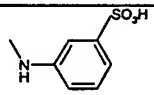
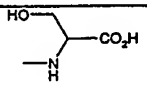
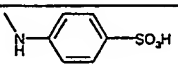
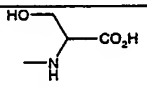
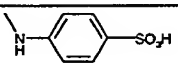
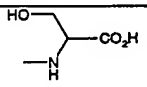
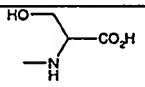
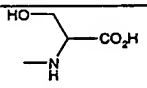
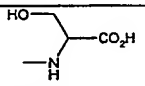
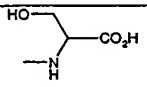
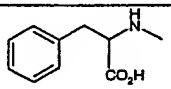
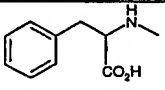
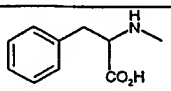
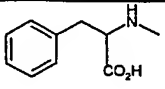
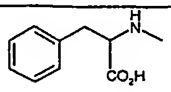
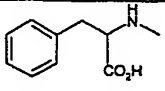
51	(125a)			0
52	(125b)			1
53	(126a)			0
54	(126b)			1
55	(127a)	-$NHCH_2CH_2OH$		0
56	(127b)	-$NHCH_2CH_2OH$		1
57	(128a)	-$N(CH_2CH_2OH)_2$		0
58	(128b)	-$N(CH_2CH_2OH)_2$		1
59	(129a)	-$NHCH_2CH(CH)_3OH$		0
60	(129b)	-$NHCH_2CH(CH)_3OH$		1
61	(130a)			0
62	(130b)			1
63	(131a)			0
64	(131b)			1
65	(132a)			0
66	(132b)			1

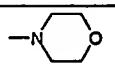
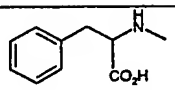
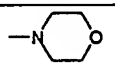
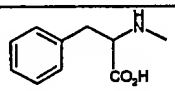
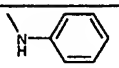
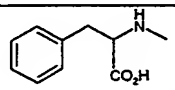
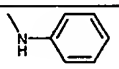
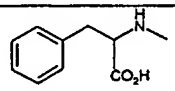
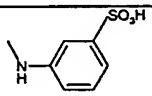
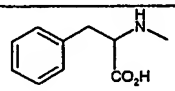
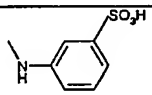
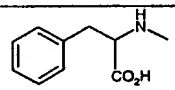
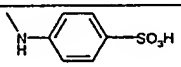
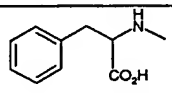
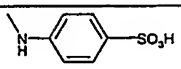
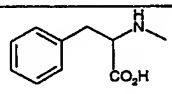
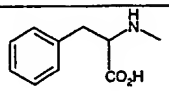
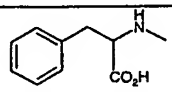
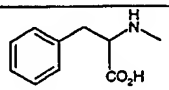
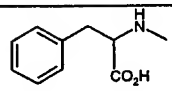
67	(133a)			0
68	(133b)			1
69	(134a)			0
70	(134b)			1
71	(135a)	-$NHCH_2CH_2OH$		0
72	(135b)	-$NHCH_2CH_2OH$		1
73	(136a)	-$N(CH_2CH_2OH)_2$		0
74	(136b)	-$N(CH_2CH_2OH)_2$		1
75	(137a)	-$NHCH_2CH(CH)_3OH$		0
76	(137b)	-$NHCH_2CH(CH)_3OH$		1
77	(138a)			0
78	(138b)			1
79	(139a)			0
80	(139b)			1
81	(140a)			0

82	(140b)			1
83	(141a)			0
84	(141b)			1
85	(142a)			0
86	(142b)			1
87	(143a)	-NHCH$_2$CH$_2$OH		0
88	(143b)	-NHCH$_2$CH$_2$OH		1
89	(144a)	-N(CH$_2$CH$_2$OH)$_2$		0
90	(144b)	-N(CH$_2$CH$_2$OH)$_2$		1
91	(145a)	-NHCH$_2$CH(CH)$_3$OH		0
92	(145b)	-NHCH$_2$CH(CH)$_3$OH		1
93	(146a)			0
94	(146b)			1
95	(147a)			0
96	(147b)			1

97	(148a)			0
98	(148b)			1
99	(149a)			0
100	(149b)			1
101	(150a)			0
102	(150b)			1
103	(151a)	-NHCH$_2$CH$_2$OH		0
104	(151b)	-NHCH$_2$CH$_2$OH		1
105	(152a)	-N(CH$_2$CH$_2$OH)$_2$		0
106	(152b)	-N(CH$_2$CH$_2$OH)$_2$		1
107	(153a)	-NHCH$_2$CH(CH)$_3$OH		0
108	(153b)	-NHCH$_2$CH(CH)$_3$OH		1
109	(154a)			0
110	(154b)			1
111	(155a)			0

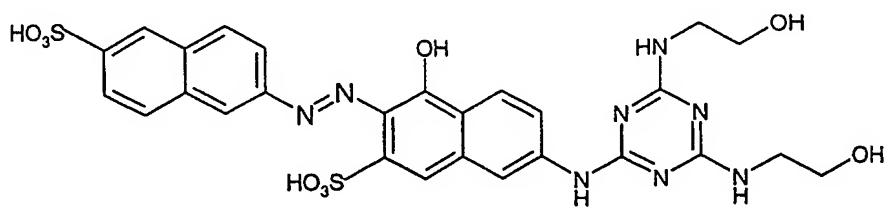
112	(155b)			1
113	(156a)			0
114	(156b)			1
115	(157a)			0
116	(157b)			1
117	(158a)			0
118	(158b)			1
119	(159a)	-NHCH$_2$CH$_2$OH		0
120	(159b)	-NHCH$_2$CH$_2$OH		1
121	(160a)	-N(CH$_2$CH$_2$OH)$_2$		0
122	(160b)	-N(CH$_2$CH$_2$OH)$_2$		1
123	(161a)	-NHCH$_2$CH(CH)$_3$OH		0
124	(161b)	-NHCH$_2$CH(CH)$_3$OH		1
125	(162a)			0
126	(162b)			1

127	(163a)			0
128	(163b)			1
129	(164a)			0
130	(164b)			1
131	(165a)			0
132	(165b)			1
133	(166a)			0
134	(166b)			1
135	(167a)	-$NHCH_2CH_2OH$		0
136	(167b)	-$NHCH_2CH_2OH$		1
137	(168a)	-$N(CH_2CH_2OH)_2$		0
138	(168b)	-$N(CH_2CH_2OH)_2$		1
139	(169a)	-$NHCH_2CH(CH)_3OH$		0
140	(169b)	-$NHCH_2CH(CH)_3OH$		1

141	(170a)			0
142	(170b)			1
143	(171a)			0
144	(171b)			1
145	(172a)			0
146	(172b)			1
147	(173a)			0
148	(173b)			1
149	(174a)			0
150	(174b)			1

(B) Synthesis of Dyes

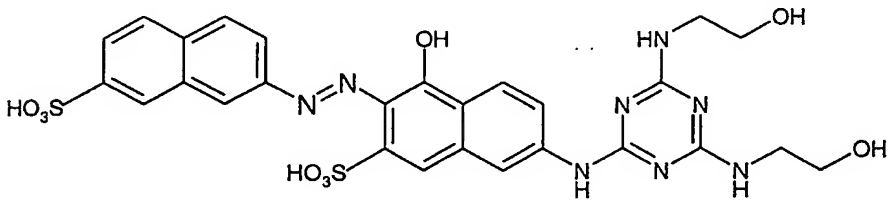
Example 151



(175)

4.5g of 2-naphthylamine-6-sulphonic acid are suspended in 150g of water and 5.7g of concentrated hydrochloric acid and the suspension treated with a total of 5ml of 4N aqueous sodium nitrite solution over 30 minutes at 0-5°C. The mixture is then stirred for a further 30 minutes and excess nitrite destroyed by addition of 3ml of 2N aqueous sulphamic acid solution. The resulting orange suspension is then added over 30 minutes at 10°C to a suspension of 11.3g of compound (100a) in 100g of water, the pH of which had previously been adjusted to 5.0 by addition of a small amount of 2N aqueous sodium hydroxide solution. During the addition, the pH is maintained at 5.0-5.5 by addition of a total of 27.9ml of 4N aqueous sodium hydroxide solution. After stirring for a further 1.5 hours at room temperature, the pH is adjusted to 8-9 to dissolve excess of the coupling component and the solution salted out by addition of 80g of sodium chloride. After stirring for a further 45 minutes, the resulting red suspension is filtered and the solids washed with a small quantity of water. After drying, there are obtained 8.2g of the compound of formula (175).

Example 152



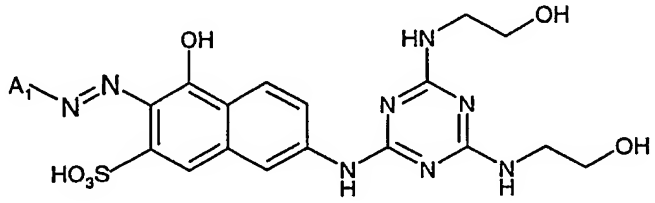
(176)

11.2g of 2-naphthylamine-7-sulphonic acid are suspended in 250g of water and 14.2g of concentrated hydrochloric acid and the suspension treated with a total of 12.5ml of 4N aqueous sodium nitrite solution over 30 minutes at 0-5°C. The mixture is then stirred for a further 30 minutes and excess nitrite destroyed by addition of 1ml of 2N aqueous sulphamic acid solution. The resulting orange suspension is then added over 1 hour at 10°C to a suspension of 22.3g of compound (100a) in 50g of water, the pH of which had previously been adjusted to 5.5 by addition of a small amount of 2N aqueous sodium hydroxide solution. During the addition, the pH is maintained at 5.0-5.5 by addition of a total of 15.6ml of 4N aqueous sodium hydroxide solution. After stirring for a further 3 hours at room temperature, the pH is adjusted to 8-9 to dissolve excess of the coupling component and the solution salted out by addition of 150g of sodium chloride. After stirring for a further 15

minutes, the resulting red suspension is filtered and the solids washed with a small quantity of water. After drying, there are obtained 30g of the compound of formula (176).

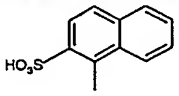
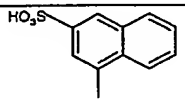
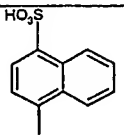
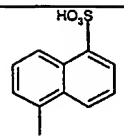
Examples 153 – 170

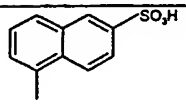
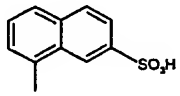
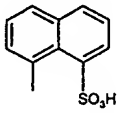
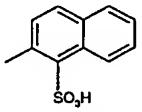
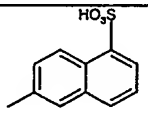
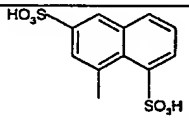
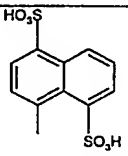
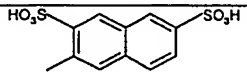
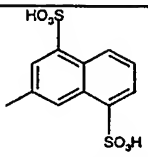
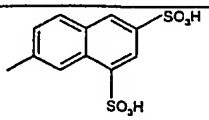
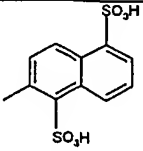
By proceeding in a manner analogous to that described in Examples 151 and 152, but replacing the 2-naphthylamine-6- or 7-sulphonic acid by an equivalent quantity of the appropriate amine, the following compounds of formula (4) are obtained, as summarized in Table 2 below.

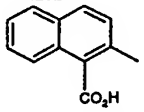
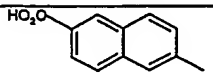
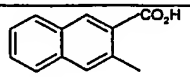


(4)

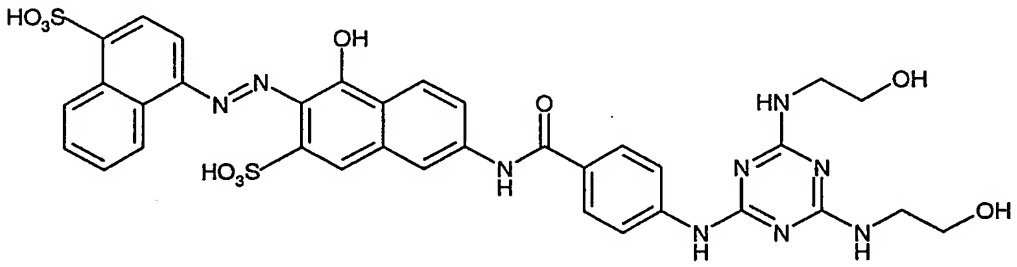
Table 2

Example Nr.	Compound Nr.	A_1
153	(177)	
154	(178)	
155	(179)	
156	(180)	

157	(181)	
158	(182)	
159	(183)	
160	(184)	
161	(185)	
162	(186)	
163	(187)	
164	(188)	
165	(189)	
166	(190)	
167	(191)	

168	(192)	
169	(193)	
170	(194)	

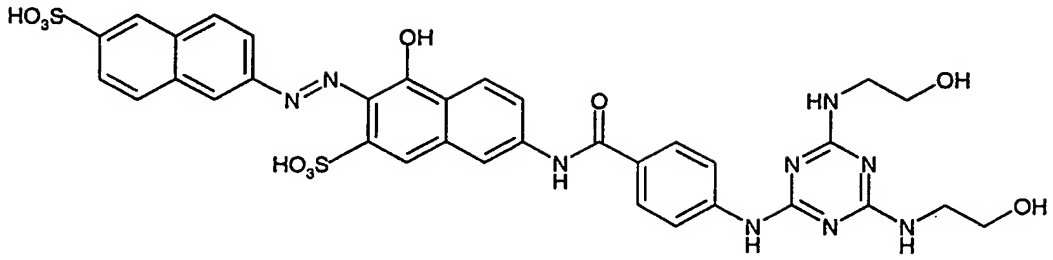
Example 171



(195)

2.3g of 1-naphthylamine-4-sulphonic acid are suspended in 100g of water and 2.9g of concentrated hydrochloric acid and the suspension treated with a total of 2.5ml of 4N aqueous sodium nitrite solution over 30 minutes at 0-5°C. The mixture is then stirred for a further 30 minutes and excess nitrite destroyed by addition of a small quantity of 2N aqueous sulphamic acid solution. The resulting suspension is then added over 35 minutes at 10°C to a suspension of 6.7g of compound (100b) in 100g of water, the pH of which had previously been adjusted to 6.0 by addition of a small amount of 2N aqueous sodium hydroxide solution. During the addition, the pH is maintained at 6.0-6.5 by addition of a total of 14.9ml of 2N aqueous sodium hydroxide solution. After stirring for a further 1 hour at room temperature, 80ml of methanol and 45g of sodium chloride are added. Stirring is continued for a further 15 minutes, the resulting red suspension is filtered and the solids washed with a small quantity of water. After drying, there are obtained 7.5g of the compound of formula (195).

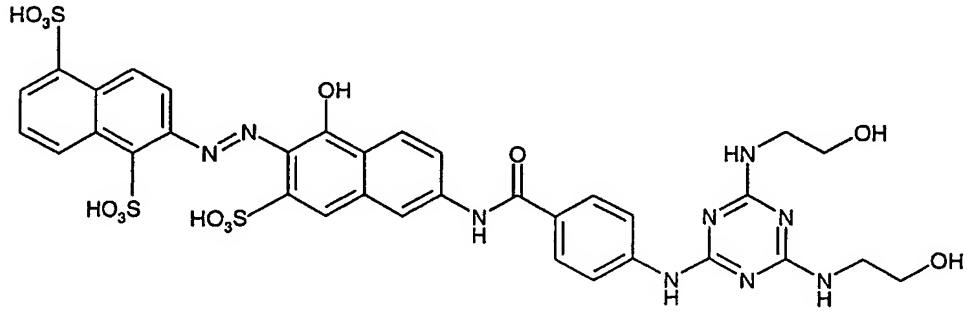
Example 172



(196)

4.95g of 2-naphthylamine-6-sulphonic acid are suspended in 100g of water and 5.7g of concentrated hydrochloric acid and the suspension treated with a total of 5.1ml of 4N aqueous sodium nitrite solution over 30 minutes at 0-5°C. The mixture is then stirred for a further 30 minutes and excess nitrite destroyed by addition of a small quantity of 2N aqueous sulphamic acid solution. The resulting suspension is then added over 1 hour at 10°C to a suspension of 13.3g of compound (100b) in 100g of water, the pH of which had previously been adjusted to 5.5 by addition of a small amount of 2N aqueous sodium hydroxide solution. During the addition, the pH is maintained at 5.0-5.5 by addition of a total of 13.2ml of 4N aqueous sodium hydroxide solution. After stirring for a further 4 hours at room temperature, 250ml of methanol and 35g of sodium chloride are added. Stirring is continued for a further 30 minutes, the resulting red suspension is filtered and the solids washed with a small quantity of water. After drying, there are obtained 11.0g of the compound of formula (196).

Example 173

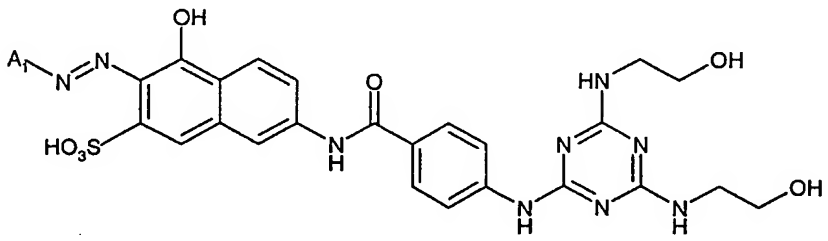


(197)

3.7g of 2-naphthylamine-1,5-disulphonic acid are suspended in 50g of water and 2.85g of concentrated hydrochloric acid and the suspension treated with a total of 2.5ml of 4N aqueous sodium nitrite solution over 30 minutes at 0-5°C. The mixture is then stirred for a further 1 hour and excess nitrite destroyed by addition of a small quantity of 2N aqueous sulphamic acid solution. The resulting suspension is then added over 40 minutes at 10°C to a suspension of 6.7g of compound (100b) in 100g of water, the pH of which had previously been adjusted to 5.0 by addition of a small amount of 2N aqueous sodium hydroxide solution. During the addition, the pH is maintained at 5.0-6.0 by addition of a total of 18.3ml of 2N aqueous sodium hydroxide solution. After stirring for a further 1 hour at room temperature, 150ml of methanol and 50g of sodium chloride are added. Stirring is continued for a further 30 minutes, the resulting orange suspension is filtered and the solids washed with a small quantity of water. After drying, there are obtained 8.2g of the compound of formula (197).

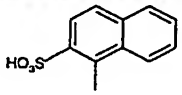
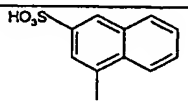
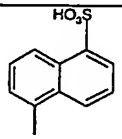
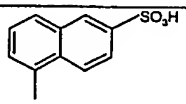
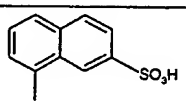
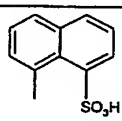
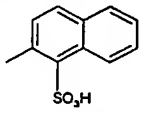
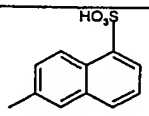
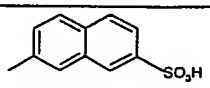
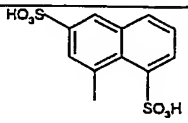
Examples 174 – 190

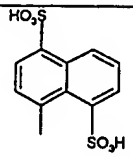
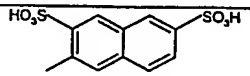
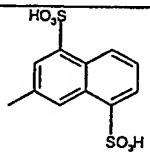
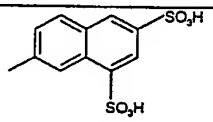
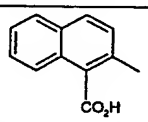
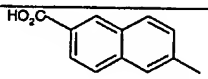
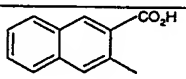
By proceeding in a manner analogous to that described in Examples 171 - 173, but replacing the 1-naphthylamine-4-sulphonic acid, 2-naphthylamine-6-sulphonic acid or the 2-naphthylamine-1,5-disulphonic acid by an equivalent quantity of the appropriate amine, the following compounds of formula (5) are obtained, as summarized in Table 3 below.



(5)

Table 3

Example No.	Coupler No.	Coupler
174	(198)	
175	(199)	
176	(200)	
177	(201)	
178	(202)	
179	(203)	
180	(204)	
181	(205)	
182	(206)	
183	(207)	

184	(208)	
185	(209)	
186	(210)	
187	(211)	
188	(212)	
189	(213)	
190	(214)	

Furthermore, by proceeding in a manner analogous to that described for the preparation of the above dyes but utilizing the intermediates (101a)-(174b) described in Table 1 together with the amines described in Examples 151-190, dyes of the corresponding formulae (4) and (5) may also be obtained.

(C) Application Examples

Examples 191-195

A mixture consisting of 50% long fibre spruce sulphite bleached and 50% short fibre beech sulphite bleached fibres is suspended in deionised water, as a 2% suspension, and refined and beaten to 22°SR (Schopper Riegler). After dewatering by means of a centrifuge and testing for dry weight, the equivalent to 10g of dry fibre are placed in a beaker and made up

to a volume of 500ml with tap water. After stirring for 1 hour, sufficient of the appropriate compound to produce a dyeing of 0.2 standard depth, based on the weight of dry fibre, as a 5g/l aqueous solution is added to the furnish suspension and stirring continued for a further 15 minutes. The suspension is made up to 700ml with water and from 300ml of the resulting suspension a hand sheet is produced using a Lhomargy sheet former. After drying on a cylinder at 90°C for 12 minutes, the CIELab coordinates and degrees of exhaustion of the dyes in the dyeings obtained are measured. The backwater ratings of the effluents are also assessed on a scale of from 1 (very highly coloured) to 5 (colourless backwater).
The results are summarized in Table 4 below.

Table 4

Example Nr.	Compound Nr.	Concentration for 0.2 St.D.	Degree of Exhaustion	Backwater rating	CIELab Coordinates
191	(175)	0.57%	87-89%	3	H* 21.4 C* 49.6 L* 62.7 *a 46.2 *b 18.1
192	(176)	0.74%	94-96%	3-4	H* 27.9 C* 55.3 L* 65.4 *a 48.9 *b 25.9
193	(195)	0.82%	86-88%	3	H* 6.8 C* 43.5 L* 57.7 *a 43.2 *b 5.2
194	(196)	0.54%	98-99%	4-5	H* 23.5 C* 52.0 L* 64.3 *a 47.7 *b 20.8

195	(197)	1.1%	79-81	2	H* 37.4 C* 56.5 L* 69.2 *a 44.8 *b 34.3